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Mono- and Binuclear Chloride and Bromide Complexes of Bi(III) with Double-Charged Cations Based on Pyridine: Syntheses and Crystal Structures

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Abstract—The reactions of solutions obtained by the reactions of Bi_2O_3 with 2 M HCl and HBr with the salts containing bis(pyridyl)alkane cations afford mono- and binuclear halide complexes $(Py\text{-}(CH_2)_3\text{-}Py)_3[Bi_2Br_9]_2$ (**I**), $(H_3O)(Py\text{-}(CH_2)_4\text{-}Py)[BiCl_6] \cdot 3H_2O$ (**II**), and $(H_2Bpp)_2[Bi_2Br_{10}] \cdot 2H_2O$ (Bpp is 1,3-bis(4-pyridyl)propane) (**III**). The structures of the synthesized compounds are determined by X-ray diffraction analysis (CIF files CCDC no. 1583338–1583340, respectively).

Keywords: bismuth, chloride complexes, bromide complexes, crystal structure

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INTRODUCTION

In spite of the fact that halide complexes are among the "classical" objects of investigation by coordination chemistry, this area continues attracting attention of researchers. For the compounds of post- and late-transition metals, this is caused, to a significant extent, by the physical properties interesting from the viewpoint of materials science, such as photocatalysis [1–4], ferroelectric properties [5–7], applicability in photovoltaic devices [8–10], and others. From the preparative point of view, these complexes are simple objects: as a rule, they are synthesized by the addition of halide salts of various metals to solutions containing anionic species $[MX_n]^{a-}$ (X = Cl, Br, I). This results in the formation of crystals, whose quality is sufficient for X-ray diffraction analysis. The main problem remaining unsolved is the search for a relationship between the synthesis conditions and the composition and structure of the anionic moiety of these compounds. This is due to the fact that some metals (especially post-transition metals, in particular, Bi(III)) are characterized by a relatively low energy of the M–X bond and the fast kinetics of ligand substitution. Owing to this, solutions containing halometallate anions can be considered as "virtual dynamic libraries" capable of forming polynuclear anions of diverse structures and compositions upon the addition of a large organic cation to the system and solid phase precipitation. It is noted that the most important factors determining the structures of the products are the properties of the solvent used and, to a higher extent, the nature of the cation [11, 12]. At the same time, although the significant body of experimental data on the structures of such compounds has been obtained within the recent years [13–18] and the overall number of deposited crystal structures exceeds 200 (for Bi(III)), it remains to be a perspective task to find correlations in this information array. Evidently, to solve this problem, one has to extend the number of described crystal structures and also to specify boundary parameters, which, in particular, can be synthesis conditions. One of the popular variants is the synthesis of halometalates in aqueous solutions of HX (X = Cl, Br, I), i.e., in an acidic medium in presence of a considerable excess of halide anions.

In this work, we synthesized and structurally characterized three new halide complexes of Bi(III): $(Py\text{-}(CH_2)_3\text{-}Py)_3[Bi_2Br_9]_2$ (**I**), $(H_3O)(Py\text{-}(CH_2)_4\text{-}Py)[BiCl_6] \cdot 3H_2O$ (**II**), and $(H_2Bpp)_2[Bi_2Br_{10}] \cdot 2H_2O$ (Bpp is 1,3-bis(4-pyridyl)propane) (**III**).

EXPERIMENTAL

Compounds **I–III** were synthesized in air. Reagents (reagent grade) were purchased from commercial sources and used as received. Bromides of bis(pyridyl)alkane cations were synthesized by the reaction of pyridine (2 equiv) and 1,3-dibromopro-